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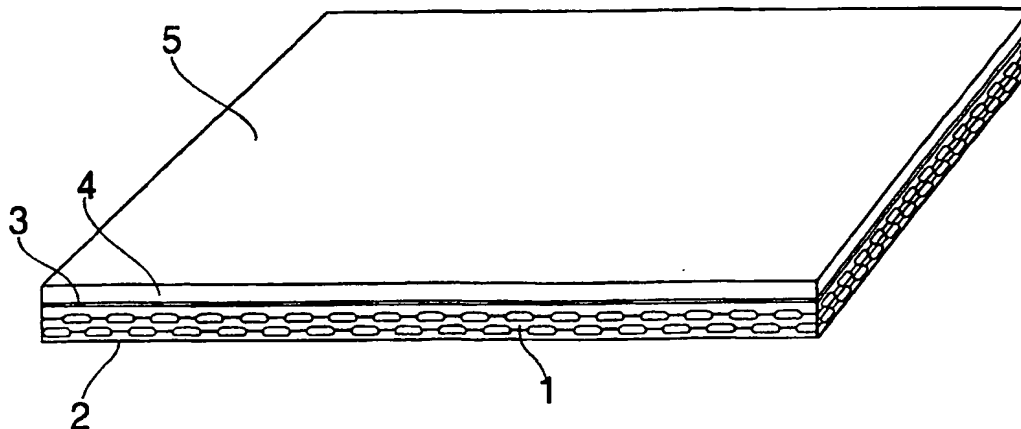
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(54) Title: NON-CURLING REINFORCED COMPOSITE MEMBRANES WITH DIFFERING OPPOSED FACES, METHODS FOR PRODUCING AND THEIR USE IN VARIED APPLICATIONS



(57) Abstract: A double-faced PTFE-silicone rubber reinforced composite with curling tendency controlled is achieved by coating one side of a balanced PTFE/glass composite with liquid silicone rubber. Each face of the composite can perform independent functions in a single application, thereby optimizing performance.



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**NON-CURLING REINFORCED COMPOSITE MEMBRANES
WITH DIFFERING OPPOSED FACES, METHODS FOR
PRODUCING AND THEIR USE IN VARIED APPLICATIONS**

5 BACKGROUND OF THE INVENTION

This invention relates to new and useful reinforced composite membranes for use in conveying, material handling, surface modifying, surface protection, and barrier applications, in which the two opposing faces of the membrane differ significantly in composition and physical characteristics, each face being constructed to perform independent functions in a given single application, thereby optimizing overall performance.

More specifically, this invention relates to reinforced composite membranes in which one face is a perfluoropolymer, such as polytetrafluoroethylene (PTFE), and the other face is an elastomer. Although the use of elastomeric materials of varied compositions is contemplated, silicone rubber is the preferred elastomeric component.

15 Polytetrafluoroethylene (PTFE) coated fiberglass fabrics and silicone rubber coated fiberglass fabrics are examples of reinforced composite membranes commonly used in many of the applications mentioned above. The two materials share several unique and valuable physical properties: flexibility, thermal stability in operating environments exceeding 350°F, and low-energy surfaces providing easy release to sticky, viscous, or adhesive materials. On the other hand, they may differ markedly in surface hardness, finish, frictional characteristics, and surface qualities difficult to specify but related to the way the surface adheres to other surfaces. PTFE has one of the lowest coefficients of friction possessed by any common material and exhibits minimal "stick-slip" behavior. On the other hand, silicone rubber, depending on its composition, finish, and hardness (durometer), often has the high coefficient of friction and pronounced stick-slip behavior or "grabby" quality typically associated with elastomeric materials.

25 The choice of whether to use a PTFE or a silicone rubber composite in a given application sometimes involves consideration of the materials' frictional and related surface characteristics. Certain applications may require a material with a low coefficient of friction, in which case PTFE composites would be expected to perform very well, while silicone rubber constructions would not. In other applications, a material with a high coefficient of friction or stick-slip characteristics may be required, in which cases a silicone rubber material would answer readily, while a PTFE construction would not.

However, in some applications, a membrane with the frictional and related surface characteristics of PTFE on one face and those of an elastomer on the other face may be needed. To address this need, efforts have been made to combine the two materials in a double-faced membrane, with PTFE on one face and silicone rubber on the opposite face. In the past, these attempts have yielded materials with a strong tendency to curl, making their handling extremely difficult and limiting their usefulness. The curling tendency is due to imbalanced stresses generated in manufacturing these composites, the result of differences in the curing characteristics, thermal coefficients of expansion, and modulae of the two components. It is the object of this invention to produce double-faced PTFE-elastomer reinforced composite membranes with curling tendency controlled to the extent that their handling characteristics and usefulness remain uncompromised.

SUMMARY OF THE INVENTION

The invention achieves a double-faced PTFE-silicone rubber reinforced composite with curling tendency controlled by coating one side of a balanced PTFE-coated glass composite with liquid silicone rubber. The composite comprises two opposing faces, wherein one face is composed of a perfluoropolymer, such as PTFE, and the other face is composed of an elastomer, such as silicone rubber. The composite consequently can perform independent functions in a single application, thereby optimizing performance.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a perspective and cut away view of an exemplary composite of the invention.

DESCRIPTION OF THE INVENTION

In accordance with one embodiment the invention, a continuous web of a glass fabric-reinforced composite, with PTFE on one face and silicone rubber on the opposite face, is produced by dip-coating, knife-over-roll coating, metering and/or wiping, and thermal curing processes.

To produce the membrane in a continuous process, woven reinforcement, which may comprise fiberglass, aramid, or other fiber able to tolerate PTFE processing temperatures and suited to the end use of the membrane, is paid off a roll and saturated and/or coated with PTFE by dipping through an aqueous dispersion or latex of the resin, removing the excess dispersion by wiping or metering, drying to remove the water, baking to remove most of the surfactant, and finally heating sufficiently to sinter or fuse the PTFE. Typically, the coating operation will be

repeated several times in order to apply the desired amount of PTFE free of cracks and other defects. Alternately, the fusing step is eliminated in the first several passes, and the multiple layers of unfused PTFE resin applied thus are smoothed and consolidated by passing the web through a calendar machine, prior to fusing and the application of one or more subsequent layers of fused PTFE resin to complete the composite. In any case, the PTFE resin is applied in such a way as to “balance” the mechanical forces or residual stresses within the PTFE resin on each coating face so that the composite lies flat and does not tend to curl. One way of achieving a balanced-coating is to apply equal amounts of PTFE to both faces and subject the faces to the same processing conditions. The coating of PTFE should be as thin as possible, while sufficient to achieve the desired function. Although a variety of coating thicknesses of PTFE to serve a variety of functions are contemplated by the invention, a coating thickness of about 1-5 mils (1 mil equals .001 in.) is preferred. All the technology involved is familiar to those skilled in the art of producing PTFE coated fabric reinforced composites, described for example in U.S. Patent No. 5,141,800 to Effenberger et al., incorporated herein by reference.

In the next step in the process, one face of the PTFE/glass composite is rendered bondable by coating with a mixture of a colloidal silica dispersion, for example DuPont Ludox® 40, and a perfluorinated copolymer resin dispersion, such as fluorinated ethylene propylene (FEP) or perfluoroalkoxy-modified tetrafluoroethylene (PFA). This is applied by dipping, wiping, drying, baking, and fusing, essentially as the PTFE dispersions were applied. Alternately, one face may be rendered bondable by treatment, under appropriate conditions and with appropriate pre- and post-treatment processing, with a mixture of sodium metal, naphthalene, and a glycol ether, or alternately, a mixture of sodium metal and anhydrous ammonia. If applicable, other means of rendering the PTFE surface bondable, for example corona treatment in special atmospheres, chemical and electrochemical treatments, metal sputtering, and vacuum deposition of metals or metal oxides, might be employed. Once again, the technology involved in applying bondable treatments to PTFE surfaces is thoroughly described in the literature and is familiar to those skilled in the art of processing PTFE films, articles, and composites of all kinds.

In the final step, the face of the PTFE/glass composite rendered bondable in the previous step is coated with a controlled amount of a relatively low viscosity (ca. 10,000 to 200,000 centipoises) platinum catalyzed, addition cure, 100 percent solids, solventless, liquid silicone rubber (LSR) formulation. The LSR coating should be as thin as possible, only as thick as necessary to achieve the desired function. Although a variety of coating thicknesses of silicone

rubber to serve a variety of functions are contemplated by the invention, a coating thickness of about 2-50 mils is preferred. The LSR formulation is composed of commercially available A and B components that are mixed in a specified ratio, typically 1:1 or 10:1. Each component contains vinyl-terminated polydimethylsiloxane polymers and may contain fumed silica as a reinforcing
5 filler, and/or extending fillers. Typically, one component, for instance the A component, contains the catalyst and the B component contains a crosslinking agent and an inhibitor that is removed by heating to allow the LSR to cure into a solid rubber. The LSR formulation may incorporate pigments and/or other additives. The membrane thus coated is completed by passing it through a coating oven or other heating device, raising the temperature of the coating sufficiently to drive
10 off or decompose the inhibitor allowing the LSR to cure into a solid rubber.

Alternately, the web may be coated with a silicone rubber incorporating an organic peroxide catalyst ("heat-curable" silicone) which may be applied from a solvent solution, dried if necessary to remove the solvent and heated appropriately to effect a cure, or with silicone rubber incorporating an atmospheric-moisture-activated acetoxycure system ("one-package" RTV),
15 once again perhaps from a solvent solution, dried if necessary to remove the solvent and allowed to remain exposed to moist air sufficiently long to effect a cure, perhaps being heated to accelerate the process.

The resulting composite is a durable, two-faced material with one face PTFE and one face silicone rubber. The composite exhibits flexural modulus about that of a plain
20 PTFE/glass fabric composite comprising the same reinforcement fabric and percent PTFE, and has little tendency to curl.

Should it be desirable, ribs, lugs, cleats, or other protuberances composed of rubber that is the same or similar in composition to the rubber face of the composite may be formed on the relatively smooth rubber face by applying beads of flowable, uncured rubber by the
25 use of robotically controlled applicators or by methods similar to those described in co-pending Application Serial No. 09/608,649, filed June 30, 2000, the subject matter of which is incorporated by reference herein. The material applied is then cured, depending on its type, according to the procedures in the paragraphs above. The rubber must be sufficiently viscoelastic to permit retention of its shape without flowing excessively during the time required to apply the
30 required number of cleats and transfer the work to an oven or other heating device or other environment in which the cure is effected.

Unlike other elastomers, silicone rubber has low surface energy. Surprisingly, the surface of silicone rubber is tacky when dry, yet very slippery when water is present on the surface. This feature of silicone rubber results in unique advantages and end uses which are contemplated by the invention.

5 FIG. 1 shows an exemplary composite of the invention in which a fiberglass reinforcement (1) is coated on both faces with PTFE (2). A mixture of a colloidal silica dispersion (3) is applied to one surface of the PTFE-coated fabric. The application of the colloidal silica dispersion (3) renders the surface bondable. The PTFE/fiberglass face rendered bondable by dispersion (3) is coated with silicone rubber (4,5) to achieve a composite with one
10 face PTFE and one face silicone rubber (5).

EXAMPLE 1

One face of a roll of commercially available PTFE/glass fabric (Chemfab Chemglas® Basic 5), containing style 2116 glass fabric as a reinforcement and comprised of about 50 percent by weight PTFE resin and 50 percent by weight glass, is rendered bondable by
15 applying a mixture of colloidal silica dispersion (DuPont Ludox® 40), PFA fluoropolymer resin solution (Dupont TE-9946), surfactants, stabilizers, and water; wiping off the excess; drying; baking; and fusing. The fabric weighs about 5.4 ounces per square yard (osy) and is about 0.005 inches thick.

Using conventional PTFE tower-coating equipment, a coating of an LSR
20 formulation composed of 50 parts by weight each of Wacker Silicones Elastosil® LR6289A and LR6289B and about 12 parts by weight of a red iron oxide masterbatch containing about 35 percent iron oxide and about 65 percent vinyl terminated silicone polymer, is applied to the bondable face of the Chemglas Basic 5. The tower is operated to provide conditions of time and temperature sufficient to cause the rubber to cure. The end result is a composite with a smooth,
25 glossy coating of silicone rubber on one face and a PTFE surface on the opposite face. The whole weighs about 7.5 osy; the silicone rubber coating is about 0.002 inches thick and is strongly adhered. The composite lays flat and can be handled easily without curling.

The example composite is fabricated into a belt for a combination weighing/packaging machine for meat and other food products. In the heat-sealing section of the
30 machine, the non-working face of the belt, i.e., the face that does not contact the product being weighed and wrapped, must slide freely over a heated platen. In another section of the machine, the wrapped package must be conveyed up an incline without slipping back. An all-PTFE belt

slides freely over the heating platen but allows the package to slip back at the incline. An all-silicone belt carries the package up the incline without slipping, but does not slide freely over the heated platen. The example belt functions optimally in both sections of the machine.

EXAMPLE 2

5 One face of another roll of the PTFE/glass fabric used in the above example is rendered bondable by treatment with a solution of sodium, naphthalene, and glycol ether. It is coated using the procedure described in Example 1, yielding a composite with physical properties almost identical to those of Example 1.

EXAMPLE 3

10 One face of a length of Chemltas 64-40916, a Chemfab product comprised of Style number 64 glass fabric saturated/coated with 40 percent by weight PTFE, is rendered bondable by application of the colloidal silica formulation as described in Example 1 and coated with 8 osy. of silicone rubber. The resulting product is fabricated into a belt 50 meters long and 1.5 meters wide. It is substituted for a conventional glass-reinforced silicone rubber belt used as a conveyor and release surface in the assembly of plastic wine bags by heat sealing. The silicone release surface of the conventional belt performs to the user's satisfaction, but the construction is difficult to drive on the user's equipment due to excessive frictional force generated when the rubber non-working face of the belt, i.e., the face that does not contact the product, slides over stationary components of the machine. The PTFE non-working face of the example belt generates minimal frictional force against the machine's stationary surfaces, allowing it to be easily driven, while the working face provides the silicone rubber release surface desired.

EXAMPLE 4

A conveyor belt with raised cleats for use in a fast-food -service toaster in which the bread products being toasted are slid across a heated platen or griddle by means of force transmitted by the moving belt, is produced as follows. A rectangle or belt "blank" of appropriate size is cut from the composite of Example 1. Using a robotic applicator, a pattern of many, identically-shaped raised cleats is laid down on the silicone rubber face of the blank. The cleats are composed of the same LSR formulation as the face itself. Each cleat is about 0.8 inches long and roughly simicircular in cross section, about 0.2 inches wide at the base and 0.04 inches high at the highest point. The longitudinal centerline of the cleat is a straight line oriented perpendicular to the direction of travel of the finished conveyor belt. The LSR forming the cleats has viscoelasticity that allows it to retain its shape during the time it takes to apply the entire

pattern of cleats. After the pattern is applied, the blank is placed in an oven operating at 500°F and allowed to remain for two minutes. When the blank is removed from the oven the silicone rubber surface bears a pattern of durable rubber cleats strongly adhered to the surface. The belt is completed by attaching lacings on two opposite ends. When installed on the toaster the cleats

5 contacting the bread products being toasted, for example hamburger rolls, are found to drive the rolls more reliably, with less slippage, than a smooth-faced belt made of similar material.

What is claimed is:

1. A fiber-reinforced flexible composite membrane having two compositionally distinct opposing faces, the membrane comprising:

a fibrous reinforcement;

5 a perfluoropolymer material coating on each side of the reinforcement, the perfluoropolymer in a balanced state having mechanical forces within the perfluoropolymer equal on each side of the reinforcement to prevent the membrane from curling; and

an elastomer disposed over the perfluoropolymer material on one side of the reinforcement.

10 2. A fiber-reinforced flexible composite membrane according to claim 1, wherein the elastomer comprises a silicone rubber.

3. A fiber-reinforced flexible composite membrane according to claim 1, wherein the perfluoropolymer comprises PTFE.

4. A fiber-reinforced flexible composite membrane according to claim 1,
15 wherein the perfluoropolymer comprises PTFE and the elastomer comprises silicone rubber.

5. A fiber-reinforced flexible composite membrane according to claim 4, wherein the reinforcement comprise a glass fiber.

6. A fiber-reinforced flexible composite membrane according to claim 1, wherein the pefluoropolymer material is applied in equal amounts to each face of the reinforcement.

20 7. A fiber-reinforced flexible composite membrane according to claim 2, wherein the silicone rubber is derived from an addition-cure, 100 percent solids, liquid silicone rubber composition.

8. A fiber-reinforced flexible composite membrane according to claim 7, wherein the liquid silicone rubber comprises one or more pigments.

25 9. A fiber-reinforced flexible composite membrane according to claim 7, wherein in the liquid silicone rubber comprises an organic peroxide catalyst.

10. A method for producing the fiber-reinforced flexible composite membrane of claim 1, comprising

a) coating a woven reinforcement able to tolerate perfluoropolymer
30 processing temperatures with the perfluoropolymer and fusing the perfluoropolymer to a woven reinforcement to obtain a balanced perfluoropolymer/woven reinforcement composite;

b) rendering one face of the perfluoropolymer/woven reinforcement composite bondable to an elastomer;

c) coating the bondable face of the perfluoropolymer/woven reinforcement composite with a low viscosity, platinum catalyzed, addition cure, solventless liquid silicone rubber elastomer; and

d) curing the liquid silicone rubber into a solid rubber.

11. The method of claim 10, wherein the liquid silicone rubber comprises two components, one component containing a catalyst and the other component containing a crosslinking agent and an inhibitor.

12. The method of claim 11, wherein the two components comprise vinyl-terminated polydimethylsiloxane.

13. The method of claim 12, wherein the two components further comprise fumed silica.

14. The method of claim 11, wherein the two components are mixed in a ratio of 1:1.

15. The method of claim 11, wherein the two components are mixed in a ratio of 10:1.

16. The method of claim 11, wherein the perfluoropolymer is applied in equal amounts to both faces of the woven reinforcement.

17. The method of claim 10, wherein the woven reinforcement is fiberglass or aramid.

18. The method of claim 11, wherein one face of the perfluoropolymer/woven reinforcement composite is rendered bondable by coating said one face with a mixture of a colloidal silica dispersion and a perfluorinated copolymer resin dispersion.

19. The method of claim 11, wherein one face of the perfluoropolymer/woven reinforcement composite is rendered bondable by treatment with a solution of sodium, naphthalene and glycol ether.

20. A conveyor belt comprising a fiber-reinforced flexible composite according to any one of claims 1-9.

21. A non-curling reinforced membrane with compositionally distinct opposed faces, the composite comprising:

a glass reinforced fabric layer having two opposed faces;

a PTFE coating applied to the fabric layer on both faces, the coating in a balanced state having mechanical forces within the PTFE equal on each side of the reinforcement to prevent the membrane from curling; and

5 a layer of silicone rubber applied to one of said opposed faces previously coated with PTFE.

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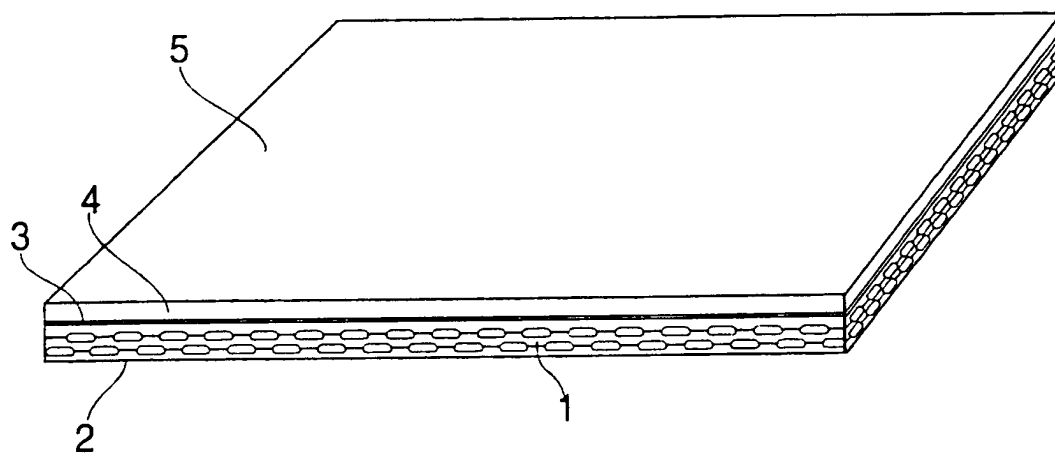


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/01733

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B32B25/20 B32B17/04 B65G15/34 B29C43/22 D06N3/18		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 B32B B65G B29C D06N		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 125 955 A (CHEM FAB CORP) 21 November 1984 (1984-11-21) page 3, line 11-58 page 4, line 3-14 figure 1 examples 1,29 claims 1,9,13 ---	1,3-6
X	US 5 217 797 A (KNOX JOHN B ET AL) 8 June 1993 (1993-06-08) column 2, line 51 -column 4, line 6 column 4, line 61 -column 5, line 6 column 5, line 42-61 column 6, line 6-13 example 1 figure 1 -----	1,2,6, 17,21
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed </div> <div style="width: 45%;"> *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *Z* document member of the same patent family </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">27 March 2001</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">07/05/2001</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Stabel, A</div>

INTERNATIONAL SEARCH REPORT

Information on patent family members

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